$LiCoO_2$ Structures by Spray Pyrolysis Technique for Rechargeable Li-ion Battery

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Summary: As the lithium-ion batteries have high energy density, Lithium-batteries have become a very attractive field of study for the researchers. Batteries' high energy density is up to the anode and cathode materials used in the batteries and the technique which is chosen for getting these materials. In this study, $LiCoO_2$, used for cathode active material in lithium ion batteries, has been prepared with spraying on a glass base by spray pyrolysis technique. $LiCoO_2$ was annealed at 600C for 3h in an air atmosphere; and crystal structures of the obtained samples were examined with XRD, the surface morphology of them was examined with SEM. Effect of annealing on crystallization has been investigated in prepared samples.

Keywords: $LiCoO_2$; li-ion battery;Spray pyrolysis

Introduction

In these days, many researchers focus on alternative energy sources such as solar cell, wind power and batteries. In the recent century many type batteries were made by the researchers. Among these batteries lithium-based batteries have a high energy density than the other batteries. The type of lithium based batteries which has the highest energy density is the lithium-ion batteries. Because of this properties lithium-ion battery technology has been very attractive field in the alternative energy sources theme. The reason of the high energy densities lithium-ion batteries is chemical reaction between the anode and cathode materials. $LiMO_2$ (M: Co, Ni, Mn, V) structure materials are used as cathode materials for lithium-ion battery. These structures tend to give Li^+ ions during the charge and tend to take Li^+ ions during the discharge [1]. Generally lithium metal is used as an anode material in lithium-ion batteries. Because of lithium metal is very reactive, it has safety problems. Lithium based metal oxides such as $LiCoO_2$, $LiNiO_2$, $LiMnO_2$... etc. are usually used as cathode material in the lithium-ion batteries. Among all cathode materials the most commonly used cathode material is $LiCoO_2$ for the lithium battery because of its high specific energy density and excellent cycle life [2]. $LiCoO_2$ forms the α-$NaFeO_2$ structure, which was a distorted rock-salt structure that the cations order in alternating (111) planes [3].Various techniques for the preparation $LiCoO_2$ have been reported in the literature. These include sol-gel, solid state, Pulsed Laser Deposition (PLD). $LiCoO_2$ powder is generally prepared by solid state technique. Solid state method is simpler and cheaper than the other technique of producing ceramic powders [9] but this method has several disadvantages such as inhomogenity, irregular morphology, large particle size, high calcinating temperature.etc [8].The performance of the battery is affected by a numerous factor such as anode and cathode particle size,components used in anode and cathode materials [4]. In recent years many researchers tried to increase $LiCoO_2$'s electrochemical properties. Because of significantly affect of the particle size on $LiCoO_2$'s electrochemical properties, tremendous research efforts are developed to reduce $LiCoO_2$ particle size using liquid solution method. In the liquid solution methods, polymeric precursors such as polyacrylic acid, citric acid were used as a chelating agent for cathode particles with good stoichiometry and morphology. [5-6-7]. Spray pyrolysis is a useful method for powder generation and is commonly used to form or process a wide variety of materials in powder form, including metals and metal oxides.[10]. In principle, it is similar to combustion where the liquid fuel was oxidized and produces gases and particles. The only difference is that spray pyrolysis produces useful powders, whereas combustion generates pollutant particles [11].

In this study $LiCoO_2$ particles were prepared by spray pyrolysis technique from spray solution. Crystal structure was investigated using XRD (X-ray diffraction) and the obtained results show a good agreement with the reported results in the literature. Surface morphology of the prepared powder was analyzed by SEM (scanning electron microscopy). SEM results reveal a uniform morphology of the particles with an average size of about 5μm.

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Result and Discussion

XRD Analysis

XRD results show that all of these samples have a $LiCoO_2$ crystallized structure. It is observed from the synthesized samples that dominant peak in 2Θ=36.63° is as (101) peak. The peaks shown with the asterisks in the Fig 1. are Co_3O_4. This result shown that obtained $LiCoO_2$ at 440ºC was not pure %100.

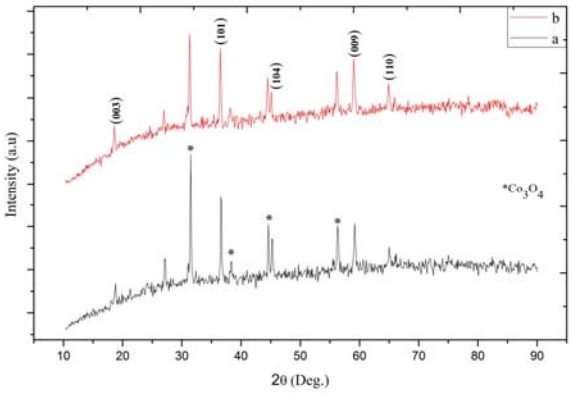

Fig. 1: XRD pattern of the samples **a)** unannealed $LiCoO_2$ **b)** Annealed $LiCoO_2$ for 3h at 600 ^oC in air

When Co^{2+} ions settle in the tetrahedral sites and Co^{3+} ions settle in the octohedral sites spinel Co_3O_4 structure is obtained. If cobalt and lithium salts react in the oxygen atmosphere it can be spinel lithium cobalt oxides of the type $Li_xCo_{3-x}O_4$ [12]. XRD result shown that LT- $LiCoO_2$ was obtained at 450°C substrate temperature.

According to XRD results, the calculated 'd' values were presented in Table 1 and these values were compared with the standard ones from JCPDS card no: 44-0145. The matching of the observed and standard 'd' values confirms that the particules are of $LiCoO_2$ with hexagonal structure. For hexagonal structure, the lattice constants 'a' and 'c' was determined by relation [14].

Table-1: Standard and observed'd' values

(hkl)	Standard d(Å)	Calculated d(Å)	
		Unannealed $LiCoO_2$	Annealed $LiCoO_2$ for 3h at 600 ^oC in air
003	4,6300	4,7264	4,7677
101	2,4080	2,4509	2,4601
104	1,9994	2,0045	2,0128
009	1,5434	1,5595	1,5634
110	1,4118	1,4330	1,4352

$$d = \frac{1}{\sqrt{\frac{4}{3a^2}(h^2 + hk + k^2) + \frac{l^2}{c^2}}}$$

were 'd' is the interplaner distance and (hkl) miller indicies, respectively.

The standard and calculated lattice constants were given in Table 2. The calculated 'a' and 'c' values are comply with standart values from JCPDS card no: 44-0145.

Table-2: Structural parameters of unannealed and annealed $LiCoO_2$.

Sample	Calculated lattice constants (Å)		
	a	c	c/a
Unannealed $LiCoO_2$	2,869	14,179	4,942
Annealed $LiCoO_2$ for 3h at 600 ^oC in air	2,851	14,303	5,016

* JCPDS card no: 44-0145 (a*= 2,824 Å c*=13,891 Å)

SEM Analysis

The avarage grain sizes of the $LiCoO_2$ particles was calculated using Scherrer formula [13].

$$D = \frac{0,9\lambda}{\beta \cos\theta}$$

Where D is mean grain size , λ- X-ray wavelength (1.5418 Å), 0.9 the crystal shape constant, Θ is the reflection angle of the peak, and β is the Corrected full width at half maximum (FWHM) of the peak in radians. The dislocation density (δ) of the $LiCoO_2$ prepared was estimated using the equation, $\delta=1/D^2$ (lines/m^2) [15-17]. The calculated D and δ values were showed in Table-3.

Table-3: Calculated "D"and "δ" values for $LiCoO_2$

Sample	D(nm)	δ x10^{14} (lines/m^2)
Unannealed $LiCoO_2$	41,46	5,82
Annealed $LiCoO_2$ for 3h at 600 ^oC in air	49,69	4,05

The grain size 'D' increased by annealing of the $LiCoO_2$ and it was obsedved that δ decreased by annealing. The dislocation density (δ) is defined as the the length of dislocation lines per unit volume is the measure of the amount of the defects in a crystal. Because dislocation density of annealed $LiCoO_2$ was lower than unannealed, the crystallity of the $LiCoO_2$ increased by annealing.

SEM images was shown in Fig 2. According to SEM images $LiCoO_2$ nano-structures were formed by spray pyrolysis technique. The fluctuations in SEM images shows that there are non-homogeneously $LiCoO_2$ particles on the glass substrate. As seen from the SEM images, distribution of particles were more homogeneous and crystallization was increased by annealing. This is comply with the XRD results.

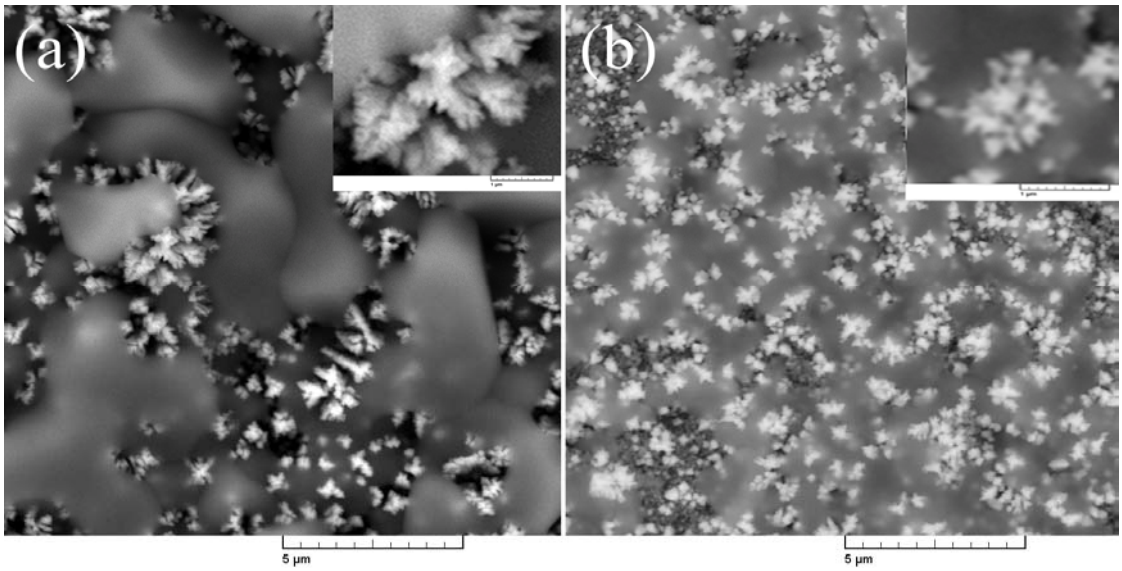

Fig 2: SEM images of the samples a) Unannealed $LiCoO_2$ b) Annealed $LiCoO_2$ for 3h at 600 ^oC in air.

Experimental

Sample Preparation

We prepared $LiCoO_2$ particles by spray pyrolysis method.First, $Co(NO_3)_2.6H_2O$ and LiCl were soluted in de-ionized water.In solution these two materials were mixed at stoichiometric ratio. Then spray solution mixed by magnetic stirrer at 1 hour.The colour of the spray solution was pink. Applied process is shown in Fig. 3.

Glass substrate was cut 1cmx1cmx1mm dimensions. The distance between substrate and nozzle set to 30cm and substrate temperature is set to 440°C and obtained solution sprayed onto glass substrate for 15 min.One of the coated glass substrate annealed for 3h in air at 600°C by box furnace. The structure of the obtained from spray solution samples were characterized by a Rigaku D/Max-IIIC diffractometer range from $2\theta=10^0$ *to* 90^0 with CuKα radiation (λ=1.5418 Å), at 30 kV and 10 mA.

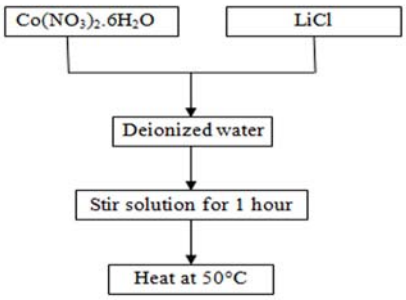

Fig 3: Schematic diagram for preparing of spray solution.

Conclusion

In this study, $LiCoO_2$ nano particles were prepared by spray pyrolysis technique. When temperature of the glass substrate was set at 450 °C, $LiCoO_2$'s crystal structure was obtained and this was confirmed by the results of XRD. 'c' and 'a',lattice parameters of obtained $LiCoO_2$, are in a compatiable with the literature and standart values of $LiCoO_2$. It was observed that the grain size was increased by the effect of annealing procedure and the dislocation density decreased as a result of that. It was also shown apparently in SEM photographs that cyristallization was increased in the end of annealing procedure. According to the SEM images of obtained samples that $LiCoO_2$ has a uniform surface morphology about 5 µm.

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